


# Red and yellow ochres from the archaeological site Pedra do Cantagalo I, in Piripiri, Piauí, Brazil

Luis Carlos Duarte Cavalcante<sup>1</sup>  ·  
Heralda Kelis Sousa Bezerra da Silva<sup>1</sup> ·  
José Domingos Fabris<sup>2,3</sup> · José Domingos Ardisson<sup>4</sup>

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**Abstract** The archaeological site *Pedra do Cantagalo I* is a sandstone shelter displaying rupestrian inscriptions. It is located in the rural area of the municipality of Piripiri, in the northern region of the Piauí state, Brazil. The site was found as being originally decorated with more than 1,900 prehistoric rupestrian paintings, along with engravings, lithics, ceramic fragments and mineral pigments forming reddish and yellowish ochres. Materials of these ochres, collected from recent excavations in this archaeological site, were analyzed by energy dispersive X-ray fluorescence (EDXRF); backscattering and transmission <sup>57</sup>Fe-Mössbauer spectroscopy at 298 K and 25 K and powder X-ray diffraction (XRD), in an effort to assess the chemical and mineralogical characteristics of these sources of pigments that composed the ancient paint materials of the site. The iron contents (expressed as Fe<sub>2</sub>O<sub>3</sub>) for the reddish ochres were found to range from ~60 to ~68 mass%; for the yellowish ochres the corresponding content was ~34 mass%, as determined by EDXRF. From the Mössbauer spectra for these red ochre samples, hematite (αFe<sub>2</sub>O<sub>3</sub>) or a mixture of hematite and goethite (αFeOOH) were identified. Actually, the spectra at room temperature for the

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✉ Luis Carlos Duarte Cavalcante  
cavalcanteufpi@yahoo.com.br

<sup>1</sup> Center of Natural Sciences, Federal University of Piauí (UFPI), 64049-550, Teresina, Piauí, Brazil

<sup>2</sup> Department of Chemistry – ICEx, Federal University of Minas Gerais (UFMG), 31270-901 Belo Horizonte, Minas Gerais, Brazil

<sup>3</sup> Federal University of the Jequitinhonha and Mucuri Valleys (UFVJM), PRPPG, Campus JK, 39100-00, Diamantina, Minas Gerais, Brazil

<sup>4</sup> Center for the Development of the Nuclear Technology (CDTN), 31270-901, Belo Horizonte, Minas Gerais, Brazil

yellow ochres are rather complex, as it is usual for most soil clay materials. At least part of the intense central doublet was assumed to be from superparamagnetic iron oxides in very small particles. The Mössbauer patterns at 25 K allowed confirming this assumption, as the superparamagnetic relaxation effects were virtually suppressed; the spectral contributions due to goethite could be thus more easily separated.

**Keywords** Prehistoric pigment · Hematite · Goethite · Mössbauer spectroscopy · Archaeometry

## 1 Introduction

The archaeological site *Pedra do Cantagalo I*, which is located in the rural area of the municipality of Piripiri (Fig. 1), in the northern region of the Piauí state, Brazil, is widely decorated with an exceptional collection of more than 1,900 rupestrian paintings (Fig. 2), along with engravings, chipped lithics, polished lithics, ceramic fragments and mineral pigments in the form of reddish and yellowish ochres [1, 2]. The rupestrian paintings mainly represent abstract figures, spear throwers, human handprints and anthropomorphic and zoomorphic motifs, in different hues of red, but also in yellow, black, gray, white, pink, wine, dark-purple and orangish. Residual charcoals found in well-structured hearths, as recently evidenced from excavations in this shelter were  $^{14}\text{C}$ -dated as being from  $1,180 \pm 30$  years before present (BP; calibrated result at 95 % probability, from 1,070 to 960 years BP).

The main purpose of this work was to analyze materials from reddish and yellowish ochres collected from scientific excavations in the archaeological site *Pedra do Cantagalo I*, in an effort to assess the chemical and mineralogical characteristics of these sources of prehistoric pigments.

## 2 Materials and methods

Four samples were collected in the scientific excavations of the archaeological site *Pedra do Cantagalo I*, in the municipality of Piripiri: two of red ochre (labeled PCI.2014.79 and PCI.2014.132) and two of yellow ochre (PCI.2014.139 and PCI.2014.145), analyzed by the following non-destructive analytical techniques: (i) energy dispersive X-ray fluorescence (EDXRF), (ii) backscattering and transmission  $^{57}\text{Fe}$ -Mössbauer spectroscopy and (iii) powder X-ray diffraction (XRD).

The X-ray fluorescence measurements of the four ochre samples were made with an energy dispersive X-ray fluorescence spectrometer, Shimadzu EDX-720, with rhodium tube and silicon-lithium detector. Data were collected under vacuum, at 40 Pa, with collimators of 5 and 10 mm.

The Mössbauer spectra were collected at room temperature ( $\sim 298$  K) with a miniaturized portable  $^{57}\text{Fe}$  Mössbauer backscattering spectrometer MIMOS II [3–5] setup in the constant acceleration mode and a  $^{57}\text{Co/Rh}$  gamma-ray source with nominal activity of about 35 mCi; spectra were also collected at 25 K with a conventional transmission setup also in the constant acceleration mode, with a  $\sim 40$  mCi  $^{57}\text{Co/Rh}$ -gamma-ray source. Maximum Doppler velocities ranged between approximately  $\pm 11.7$  and  $\pm 12.4$  mm  $\text{s}^{-1}$ , respectively. Mössbauer isomer shifts are quoted relatively to an  $\alpha$ -Fe foil at room temperature. The experimental data were fitted with Lorentzian functions by least-square fitting with WinNormos<sup>TM</sup> for Igor Pro<sup>TM</sup> software version 6.1.



**Fig. 1** Geographical maps showing the location of the municipality of Piripiri and of the archaeological site Pedra do Cantagalo I

The powder X-ray diffraction (XRD) patterns were collected in an equipment Rigaku model D/Max Ultima Plus set to a current of 30 mA and a voltage of 40 kV, with the  $\text{CuK}\alpha$  ( $\lambda = 1.541838 \text{ \AA}$ ) radiation, at a scan rate of  $1^\circ 2\theta \text{ min}^{-1}$ , from  $4^\circ$  to  $80^\circ 2\theta$ . Silicon was used as an external standard.

### 3 Results and discussion

The results of the elemental chemical composition (Table 1), as determined by X-ray fluorescence, showed that the iron contents (expressed as  $\text{Fe}_2\text{O}_3$ ) in the reddish ochres are 68.11(9) mass% and 59.72(4) mass%, respectively, corresponding to the PCI.2014.79 and PCI.2014.132 samples; for the yellowish ochres the corresponding contents are 33.87(3) mass% and 34.11(9) mass%, respectively for the PCI.2014.139 and PCI.2014.145 samples.



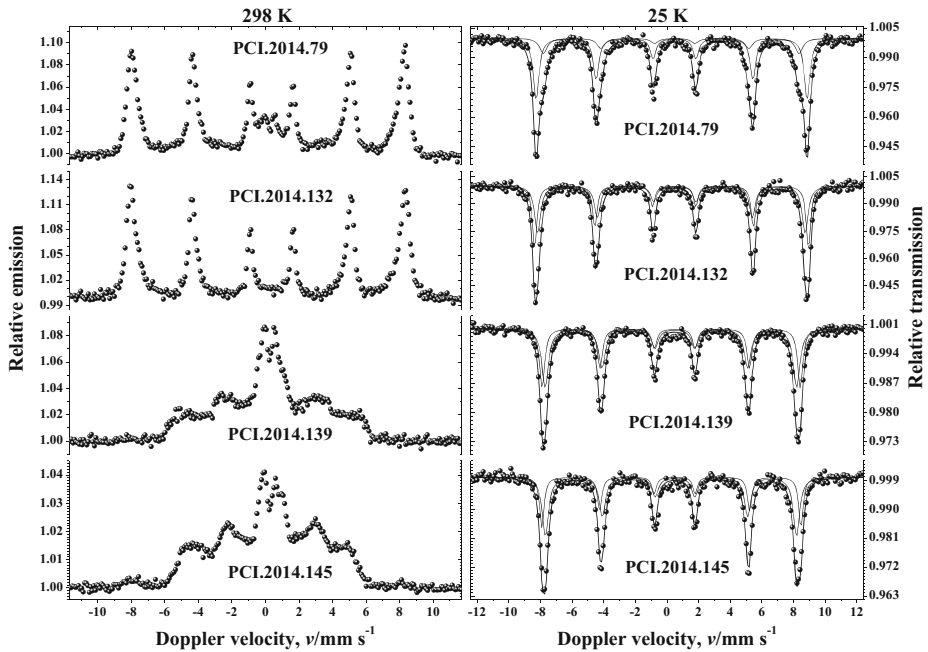
**Fig. 2** Details of the rupestrian paintings from the archaeological site Pedra do Cantagalo I

**Table 1** Chemical composition for the four ochre samples, as determined by X-ray fluorescence spectroscopy

	Oxides content/mass%			
	PCI.2014.79	PCI.2014.132	PCI.2014.139	PCI.2014.145
Fe <sub>2</sub> O <sub>3</sub>	68.11(9)	59.72(4)	33.87(3)	34.11(9)
SiO <sub>2</sub>	24.7(1)	32.2(1)	50.6(1)	49.1(1)
Al <sub>2</sub> O <sub>3</sub>	5.5(1)	4.91(9)	10.01(9)	13.0(1)
SO <sub>3</sub>	0.99(4)	0.49(1)	0.72(1)	1.00(1)
P <sub>2</sub> O <sub>5</sub>	0.46(3)	1.50(2)	2.03(9)	1.62(9)
K <sub>2</sub> O	0.06(1)		0.565(6)	0.140(5)
CaO			0.147(9)	0.166(6)
TiO <sub>2</sub>		0.759(9)	1.32(1)	0.720(8)
MnO	0.18(1)	0.198(4)	0.032(9)	0.076(3)
V <sub>2</sub> O <sub>5</sub>		0.085(9)		0.035(4)
Cr <sub>2</sub> O <sub>3</sub>		0.074(9)		
ZrO <sub>2</sub>		0.064(9)	0.236(9)	
BaO			0.46(2)	
Y <sub>2</sub> O <sub>3</sub>			0.010(1)	
ZnO				0.016(1)
CuO				0.017(1)

The number in parentheses are uncertainties over the last significant digit, as provided by the spectrometer

From the Mössbauer spectra (Fig. 3; corresponding hyperfine parameters in the Table 2) for these red ochres, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) or a mixture of hematite and goethite ( $\alpha$ -FeOOH) were identified. Actually, the spectra at room temperature for the yellow ochres are rather complex, as it is usual for most soil clay materials. The intense central doublet could be alternatively assumed to be resulting from superparamagnetic iron oxides in very small



**Fig. 3** 298 K-backscattering and 25 K-transmission  $^{57}\text{Fe}$ -Mössbauer spectra for the four ochre samples

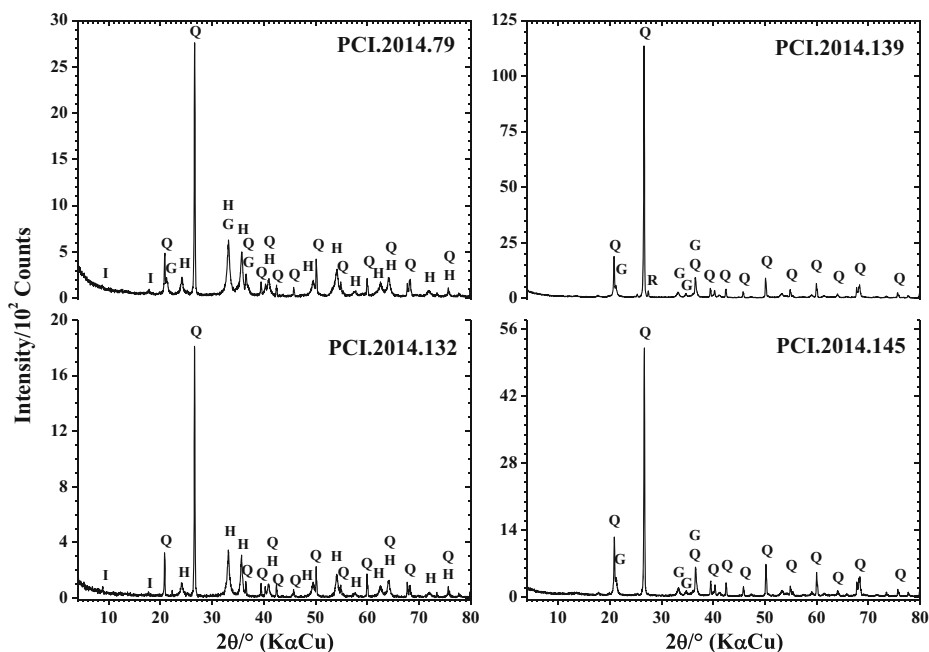
**Table 2** Parameters from fitting  $^{57}\text{Fe}$  Mössbauer spectra recorded at 25 K, for the four ochre samples

Sample	Fe site	$\delta/\text{mm s}^{-1}$	$\varepsilon/\text{mm s}^{-1}$	$\Gamma/\text{mm s}^{-1}$	$B_{hf}/\text{T}$	RA/%
PCI.2014.79	Hematite	0.48(1)	-0.18(1)	0.43(1)	53.11(2)	69.1(5)
	Goethite	0.48(1)	-0.23(2)	0.58(3)	50.11(9)	30.9(5)
PCI.2014.132	Hematite	0.47(1)	-0.16(1)	0.34(3)	53.67(7)	43(2)
	Hematite	0.48(1)	-0.22(1)	0.45(2)	52.4(1)	57(2)
PCI.2014.139	Goethite	0.47(1)	-0.22(1)	0.39(3)	50.6(1)	36.7(9)
	Goethite	0.47(1)	-0.25(1)	0.51(4)	49.3(1)	63.3(9)
PCI.2014.145	Goethite	0.48(1)	-0.20(1)	0.33(3)	50.77(7)	29.2(1)
	Goethite	0.47(1)	-0.26(1)	0.48(2)	49.21(7)	70.8(7)

$\delta$  = isomer shift relative to  $\alpha$  Fe;  $\varepsilon$  = quadrupole shift;  $\Gamma$  = line width;  $B_{hf}$  = magnetic hyperfine field; RA = relative subspectral area. The number in parentheses are uncertainties over the last significant digit, as it was estimated from the least-squares fitting algorithm.

particles. The Mössbauer patterns at 25 K allowed confirming this assumption, as the superparamagnetic relaxation effects were virtually suppressed; the spectral contributions due to goethite could be thus more easily separated.

Figure 4 shows the powder XRD patterns for the four ochre samples. All crystalline phases were identified by comparing with the corresponding data from JCPDS [6] standards. The diffraction patterns for the red ochres evidenced characteristic Bragg reflections of quartz ( $\text{SiO}_2$ ; JCPDS card # 46-1045), hematite (card # 33-664), goethite (card # 29-713)



**Fig. 4** Powder XRD patterns for the four ochre samples. Q = quartz, H = hematite, G = goethite, I = illite, R = rutile

and illite ( $(K, H_3O)Al_2Si_3AlO_{10}(OH)_2$ ; card # 26-911). The diffraction patterns for the yellow ochres exhibited reflections corresponding to quartz (card # 46-1045), goethite (card # 29-713) and rutile ( $TiO_2$ ; card # 21-1276).

## 4 Conclusions

Samples from ochre, the source of mineral pigments of the paintings used to make the prehistoric rupestrian paintings of the archaeological site *Pedra do Cantagalo I*, were found to be composed by iron oxides as principal chromophores: hematite or a mixture of hematite and goethite, for the red, and by far dominantly goethite, for the yellow. Additionally to these main iron-bearing species, the archaeological materials were also found to contain quartz, illite and rutile. These results underline the usefulness of an integrated set of analytical techniques, which may be understood as laboratory archaeometric tools, particularly Mössbauer spectroscopy, in approaching the problem of identifying, characterizing and quantifying iron-bearing minerals in materials from the archaeological heritage.

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